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Rapid and on-site simultaneous electrochemical detection of copper, lead and mercury in the Amazon river

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Abstract

In poor and remote zones of the world, such as the Amazon region, the lack of analytical infrastructures prevents regular quality assessments of water systems. The access to affordable, portable and robust analytical technologies for real-time and on-site water monitoring is, therefore, key to safeguard vulnerable communities and the environment. In this context, we have developed and successfully implemented an electrochemical methodology for the rapid (60 s) and effective simultaneous electrochemical detection of heavy metal ions of concern (Pb^{2+} , Cu^{2+} and Hg^{2+}) in water, with a single screen-printed electrode probe. In particular, we show a wide quantification range for each pollutant (5-300 $\mu\text{g L}^{-1}$), and detection limits below the Environmental Protection Agency (EPA) maximum contaminant levels for drinking water: 0.015, 1.3 and 0.002 mg L^{-1} for Pb^{2+} , Cu^{2+} and Hg^{2+} , respectively. The electrochemical sensors were tested in high temperature and humidity conditions in remote areas of the Amazon river, highly affected by mining-related heavy metal pollution. The field measurements were validated against standard lab-based analytical methods, showing excellent agreement. Our methodology can lead to an affordable and portable diagnostic tool for rapid and on-site monitoring of heavy metals pollution in remote areas.

Keywords: Screen-printed electrodes; Electrochemical sensor; Heavy Metals; Water; Amazon

1. Introduction

Access to safe water is fundamental to human development and well-being [1]. Water quality control is, therefore, indicated as a key priority in the 6th and 14th Global Goals for Sustainable Developments for a better world [2]. In poor and remote areas of the world, however, adequate water quality monitoring is hindered by the lack of proper infrastructures for analytical measurements and/or the prohibitive cost of most detection tools.

As a result, in areas such as the Amazon, appropriate water quality control is a challenge. The development of cost-effective and portable analytical technologies is, therefore, critical to prevent any risks to public health and to assist with the definition of *ad hoc* water policies and regulations [3]. Despite the unique flora and fauna and great biodiversity of the Amazon region [4], the quality of the water of the Amazon river is seriously compromised [5-8]. The area is subject to irresponsible anthropogenic activities, including intense mining extractions of gold [6, 7], negligently carried out at the unlicensed so-called artisanal and small-scale gold mining (AGSM), which is the cause of severe heavy metal contamination, in particular by mercury. [7, 9].

Typical environmental monitoring methods require multiple steps, including sample collection, storage, transportation and treatment, prior to being analysed in centralised laboratories. The long-time delays associated with these processes, may result in inevitable loss and degradation of analytes, due to chemical, biological and physical reactions [10], thus compromising the analytical quality of the measurements. These processes are also impracticable in extreme or remote locations, due to the lack of proper analytical infrastructures in close proximity. Development and implementation of a suitable and cost-effective technology to monitor heavy metals in the field becomes, therefore, necessary to allow more accurate and rapid analytical data collection [11]. Several commercial kits are currently available for heavy metals detection, based on colorimetric methods (e.g. Sensafe®Water Metal Check). Although

cost-effective, rapid and easy-to-use, these kits provide qualitative measurements only. More advanced colorimetric-based sensors for heavy metals, using microfluidic paper-based analytical devices (μ PADs), have been reported [12]. Such systems require, however, image digitalisation and analysis to perform the quantification, which might be challenging for field implementation in remote areas. Optical chemical sensors allow much higher sensitivity and selectivity, due to the deployment of molecular recognition probes that enhance their detection ability [13], but are also impractical for real-time monitoring. On the other hand, a portable X-ray fluorescence spectrometer (pXRF) has demonstrated its suitability for in-situ determination of heavy metals in water [14]. Despite its robustness, comparable to other spectrometric and spectroscopic analytical techniques, such as ICP-MS, ICP-OES or AAS, both the cost of the technology and the high detection limits limit their practical application.

Electrochemical-based measurements present several advantages that overcome the limitation of these heavy metals detection systems [15]. In particular, stripping voltammetry methods can be considered as a powerful technique for field analysis of heavy metal ions, due to the small size of the equipment, easy installation, accurateness, sensitivity and the possibility of multi-analyte detection [16-21]. The use of screen-printed electrodes (SPEs) as electrochemical electrodes for the environmental monitoring of heavy metals has gained popularity over the past decade because of low cost (mass-production), disposability (avoiding tedious pre-treatment steps), versatility and suitability for real-time sensing and, depending on the technique used, ease-of-operation by unskilled users [22]. The individual detection of heavy metals by SPEs, with low limits of detection demanded by environmental regulations, has been already successfully demonstrated. Many types of SPEs have been reported for this purpose, including mercury-coated SPEs, bismuth-coated SPEs, gold-coated SPEs, chemically modified and unmodified carbon-SPEs and enzyme immobilised SPEs [23]. The simultaneous detection of heavy metals, such as Pb^{2+} , Cd^{2+} , Cu^{2+} and Zn^{2+} by SPEs has also been reported [23]. Nonetheless, the concomitant detection of several heavy metals in the presence of Hg^{2+} by SPEs remains a

challenge. The reason for this is the particular experimental conditions needed for the detection of this pollutant, such as an acidic medium and the presence of chloride [24]. The different levels at which Hg^{2+} and other heavy metals can be found in the environment makes the establishment of a reliable method for simultaneous detection difficult. To the best of the authors' knowledge, there is only one example so far of simultaneous determination of Pb^{2+} , Cu^{2+} and Hg^{2+} in spiked fuel bioethanol samples by SPEs [25], which involves analysis in a matrix completely different from water, i.e. organic-hydroethanolic solutions.

With the aim of overcoming the limitations of analytical techniques currently available and achieving the real time and on-site water quality monitoring, we report here an innovative methodology for the rapid and simultaneous quantitative detection of lead, copper and mercury in water. These metals were chosen because of their incidence in Colombian rivers, and particularly in the Amazon river, due to artisanal gold mining and other anthropogenic activities. We use screen printed gold electrodes (Au SPEs) and optimise deposition potential and time for square-wave anodic stripping voltammetry-based analyses. The effect of the electrolyte on the measurements is also investigated for the first time. Finally, we test our methodology in field, on non-pre-treated water samples from the Amazon river in Colombia. In this way, we assess the influence that any interference in water, as well as extreme temperature and humidity conditions characteristic of the Amazon region, might have on the reliability of the measurements.

Our work seeks to demonstrate the applicability of electroanalytical technologies beyond proof-of-concept with a transition from lab-based optimisation to field implementation of the methodology developed, paving the way for an innovative and affordable route to water quality monitoring that can safeguard communities in remote areas of the world from the use of unsafe water.

2. Material and Methods

2.1. Chemicals and solutions

Lead, copper and mercury standards for ICP (1000 mg L⁻¹), hydrochloric acid (37 %), redistilled nitric acid (70 %) and sulphuric acid (95-98 %) were acquired from Sigma-Aldrich, UK. All aqueous solutions were prepared using high-purity deionised water ($R \geq 18.2 \text{ M}\Omega \text{ cm}$) obtained from a Milli-Q water purification system (Millipore, USA). Working multi-standard solutions of heavy metals were prepared just before use by an appropriate dilution of stock solutions, and were adjusted to pH 2 with HNO₃. All chemicals used were of analytical grade without any further purification. Note that diluted standard solutions and acid solutions required to perform on-site analysis were previously prepared in the lab and transported to the field under constant refrigeration ($\sim 4 \text{ }^{\circ}\text{C}$).

2.2. Instrumentation

Square wave anodic stripping voltammetry (SWASV) measurements were performed by using either a hand-held battery powered PalmSens3 (Palm Instruments BV, The Netherlands) connected via USB to a laptop with PSTrace 5.3 software, or a hand-held battery powered PalmSens4 potentiostat (Palm Instruments BV, The Netherlands) communicated *via* Bluetooth with PSTouch app on an Android smartphone. Screen-printed electrodes (SPE) DRP-220BT (DropSens, Spain), consisting of a low temperature-curing gold ink working (4 mm diameter) and counter electrodes, and a silver pseudo-reference electrode, were used. Analogous screen-printed electrodes with a high temperature-curing gold ink electrode (DRP-220AT) were also tested in this work.

Small glass beakers (10 mL) and plastic containers (with internal volume of 25 mL) were used for the electrochemical analysis. Voltammetric measurements, either in the lab or in the field, were performed by placing the screen-printed gold electrodes vertically into the electrolyte solution, allowing convenient stirring or mixing and spiking of solution to perform

standard addition methods. Figure 1 illustrates the fabrication process of screen-printed gold electrodes and the methodology for electrochemical analysis of heavy metals in water.

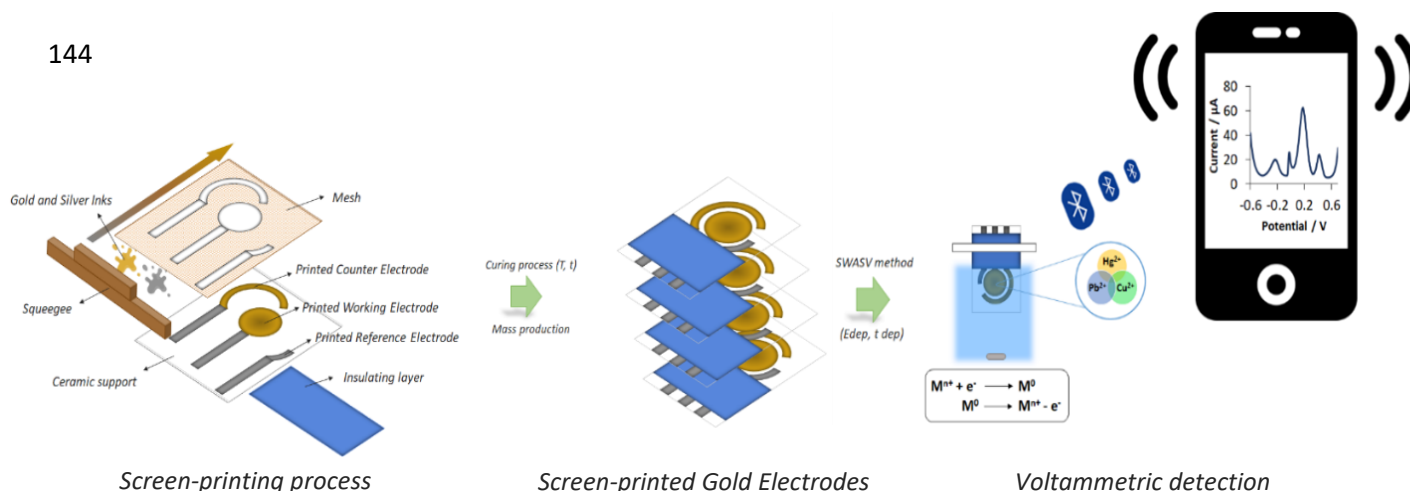


Figure 1. Scheme of the fabrication process of screen-printed gold electrodes and detection principles of heavy metals in water. Data is recorded with a potentiostat and transferred to a mobile device via a wireless connection.

Microscopic images of the surface of screen-printed gold electrodes were obtained by Field Effect Scanning Electron Microscopy (FESEM) using a FE SEM S-4800 instrument (Hitachi, USA).

2.3. Electrochemical measurements

The SPE was placed into the cell and the conditioning of the surface was performed to obtain a proper baseline and a stable response. For that, five cycles of cyclic voltammetry (CV) were applied between -0.1 and +0.8 V, at a step potential of 4 mV, a conditioning potential of +0.7 V for 15 s and a scan rate of 50 mV s⁻¹ in 0.1 mol L⁻¹ HCl, as previously described [24]. Then, 10 mL of water sample was placed in the cell and the SWASV measurement was carried out. The optimised SWASV method was carried out under the following conditions: conditioning potential, +0.7 V for 15 s; deposition potential, -0.6 V for 60 s (under stirring, 600 rpm) or 300 s

(under no stirring); equilibration time, 10 s; amplitude, 40 mV; step potential, 6 mV; and frequency, 20 Hz. Initial and final potentials were -0.6 V and +0.7 V, respectively. This range was chosen by taking into account the peak potential values for the three target metals, while avoiding the hydrogen evolution reaction (occurring at ca. -0.8 V). Note that all the potentials applied throughout this work are referred to Ag pseudo-reference electrode.

All voltammetric measurements were performed in 0.1 mol L⁻¹ HCl as electrolyte, unless otherwise stated. Consequently, the chloride concentration of the water samples directly collected from the Amazon river was adjusted in the field by adding the appropriate amount of concentrated HCl.

All electrochemical analyses were carried out in the presence of dissolved oxygen (no de-aeration was needed). Bulk stripping voltammetric signals (without blank subtraction) were used for peak current measurements. Both in the lab and in the field, simultaneous heavy metals quantification was performed by standard addition method. All voltammetric measurements were performed with at least three different SPEs. The limits of detection (LOD) and quantification (LOQ) were calculated as 3 x SD/m and 10 x SD/m, respectively, in which SD is the standard deviation of blank samples (n = 8) and m is the slope of the calibration curve.

2.4. Field tests

The field tests were performed around the area of Leticia, which is the capital of the Department of Amazonas in Colombia (4°12'19"S 69°55'58"W) and one of the major ports in the Amazon river, located at the border triangle of Colombia, Brazil and Peru (Figure S1A). Water sampling and analysis in the field were performed in March during the rainy season in the Amazon rainforest, when the team was available for travelling. Two sampling points were selected (Figure S1B), which corresponded respectively to the indigenous community of Aguila (4°13'16"S 69°56'42"W) in the city of Leticia, and Santa Sofia (4°00'43"S 70°08'13"W) in a remote area. Surface water samples were collected by the spot sampling method. Sampling was carried

out at approximately 200 m from the river bank to avoid local contamination by domestic activities. The tests were performed with the consensus and the participation of the indigenous communities.

For heavy metals detection, water samples were collected in 50 mL polyethylene tubes and electrochemically assayed as described above. Standard physicochemical parameters (temperature, pH, dissolved oxygen and conductivity) at the sampling points were also measured by directly immersing the sensing probe (HQ40D, Hach, U.S.) in the water at a depth of approximately 40 cm. Table 1 summarises the physicochemical parameters measured *in-situ* at the sampling points in the Amazon River. Note that the low oxygen concentration in the water sample from the Santa Sofia site is due to the partially stagnant flow conditions at the sampling point, while the Aguila site showed oxygen concentrations close to saturation levels.

Table 1. Physicochemical parameters measured in-situ at the sampling points of Aguila and Santa Sofia, Amazon River

	Aguila	Santa Sofia
pH	6.6	5.9
Conductivity ($\mu\text{S cm}^{-1}$)	10.9	11.6
Dissolved oxygen (mg L^{-1})	9.5	3.9
Temperature ($^{\circ}\text{C}$)	26.9	27.0

Validation of the electrochemical measurements were performed by using inductively coupled plasma optical emission spectroscopy (ICP-OES iCAP 6500, Thermo Fisher Scientific, U.S) and cold vapour atomic absorption (CV-AA)) at the Integrated Laboratory of Civil and Environmental Engineering, Universidad de Los Andes, Bogotá (Colombia). For these analyses, water samples were collected from the surface of the Amazon river in specific plastic and/or

glass vessels, according to standard water sampling protocols [26]. During the sampling stage, powder-free nitrile gloves were used to avoid external contamination of the water. The water samples did not undergo any pre-treatment rather than standard preservation methods to ensure the integrity of the samples collected for the validation analyses [26]. The collected samples were stored in cold ($\sim 4^{\circ}\text{C}$) inside portable polystyrene iceboxes by using ice and cold packs, and promptly transported from the Amazon to the Water Environmental Laboratory at Universidad de los Andes in Bogotá (Colombia) for validation analyses.

3. Results and Discussion

3.1. Optimisation of the voltammetric detection method

The aim of this study was to develop a reliable method for the real-time simultaneous determination of Pb^{2+} , Cu^{2+} and Hg^{2+} in a high pollution scenario (the Amazon river). Screen-printed gold electrodes were implemented for this purpose. Gold-based screen-printed sensors have demonstrated their applicability for the individual determination of these heavy metals by voltammetry [27], despite the limited potential window of gold compared to other metal-based electrodes [25]. Nevertheless, the simultaneous detection of several metal ions by Au SPEs has not been demonstrated yet.

In this study, the square wave anodic stripping voltammetry method is proposed because of the high analytical sensitivity of stripping techniques, which makes them suitable for the simultaneous detection of trace heavy metals in environmental water[15].

We tested two types of Au SPEs, which differed in the curing temperature for the gold electrode, indicated either as high or low temperature (exact temperature values not disclosed by the manufacturer). Figure 2 reports the SEM images of the two electrodes. As shown, the electrode cured at low temperature (Au SPE-LT) is characterised by a higher roughness. The gold electrode cured at high temperature (Au SPE-HT) demonstrated to be unfeasible for the

determination of Pb^{2+} (deposition potential ~ -0.5 V), and for a reliable detection of Cu^{2+} (deposition potential ~ 0.0 V). As shown in Figure S2A, the application of negative deposition potentials leads to undesirable peaks (at -0.4 V and -0.2 V) in the voltammogram of the blank sample, which clearly affect the performance of Au SPE-HT. In fact, when such negative potentials were applied on Au SPE-HT, a subsequent drastic reaction of the gold surface towards the hydrogen evolution was observed, which caused the total degradation of the electrode surface, making it no longer usable (Figure S2B). Consequently, only Au SPE-LT demonstrated to cover the potential window between -0.6 V to $+0.7$ V (Figure S2A), required for the display of three separated voltammetric peaks corresponding to the three metals targeted in this study. A similar result has been previously observed in hydroethanolic solutions [25], where Au SPE cured at high temperature showed a narrower potential window in the negative potential region (up to -0.3 V) limiting the sensitive determination of Pb^{2+} . Thus, it is confirmed that the curing temperature of gold surfaces during SPE fabrication has an impact on electrochemical performance. Consequently, only Au SPEs cured at low temperature were used for further experiments.

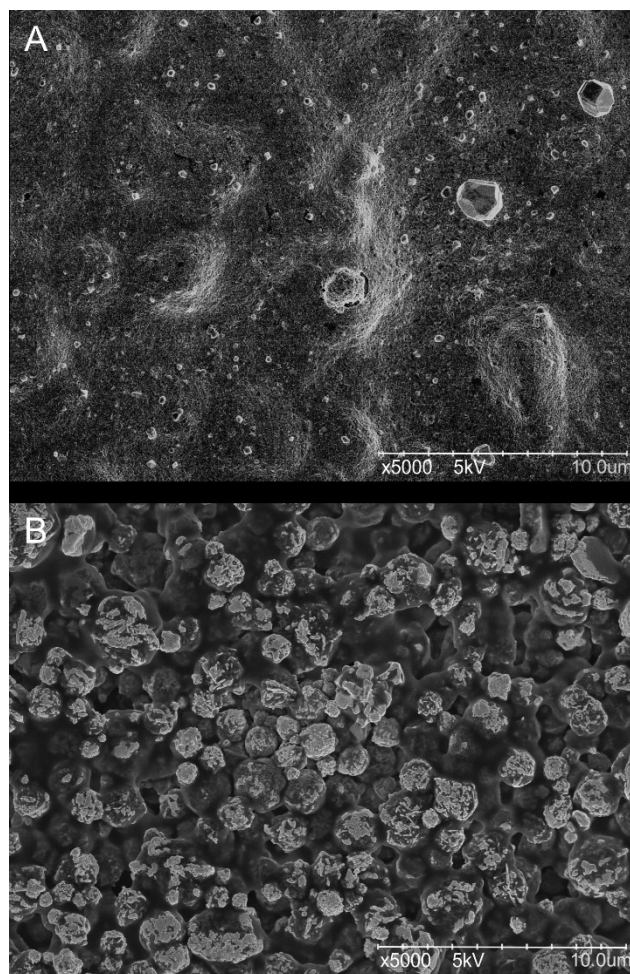


Figure 2. SEM images recorded for screen-printed gold electrodes cured at high-temperature, Au SPE-HT (A) and cured at low temperature, Au SPE-LT (B).

The most favourable deposition potential and time for the simultaneous detection of Pb^{2+} , Cu^{2+} and Hg^{2+} by square-wave anodic stripping voltammetry (SWASV) was subsequently investigated. Other instrumental parameters, such as step potential, amplitude and frequency, were instead kept constant at 6 mV, 40 mV and 20 Hz, respectively, according to analogous values previously reported for the individual detection of these metal ions, by using different Au SPEs [24, 25, 27, 28]. The potential deposition was evaluated between -0.6 V and +0.4 V, using $50 \mu\text{g L}^{-1}$ of each metal in 0.1 mol L^{-1} HCl as electrolyte. As shown in Figure 3, the analytical response to Cu^{2+} was the most significantly influenced by the potential deposition. The current

intensity remained instead more stable for Pb^{2+} and Hg^{2+} over the tested applied potentials. Considering the high sensitivity showed by Cu^{2+} and the overall stability of Hg^{2+} signal, the optimal value of deposition potential was selected in favour of the response to Pb^{2+} , which showed larger variations in its performance, compared to the other two analytes. Therefore, according to the maximum current value obtained for Pb^{2+} , a deposition potential of -0.6 V was chosen for further experiments.

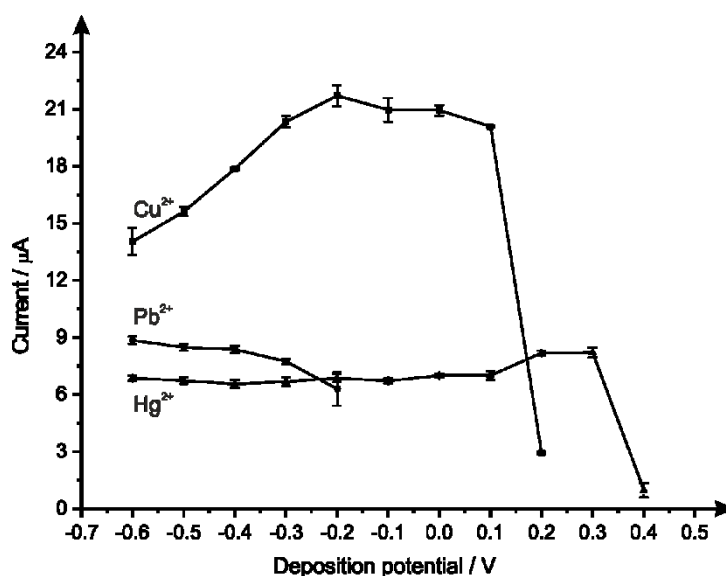


Figure 3. Evaluation of deposition potential between -0.6 V and +0.4 V on SWASV responses of $50 \mu\text{g L}^{-1}$ of Pb^{2+} , Cu^{2+} and Hg^{2+} in $0.1 \text{ mol L}^{-1} \text{ HCl}$. SWASV conditions: +0.7 V for 15 s conditioning step; 60 s deposition time; 40 mV amplitude; 6 mV step potential; 20 Hz frequency; 10 s equilibration time; 600 rpm stirring speed. Analysis were performed in triplicate ($n = 3$)

The influence of the deposition time (between 30 s and 300 s) on the Pb^{2+} , Cu^{2+} and Hg^{2+} voltammetric responses was subsequently tested. As expected, the peak currents increased with increasing accumulation times, however, contrarily to what usually happens with other electrodes, no plateau was reached for high deposition times. As shown in Figure 4, Cu^{2+} underwent the largest changes in the current, with an improvement in the peak shape while increasing the deposition time, even though standard deviations of the measurements were

significantly higher for deposition times over 180 s. Smaller changes were observed in the voltammetric responses of Pb^{2+} and Hg^{2+} compared to Cu^{2+} . In both cases, voltammetric peaks became distorted at 300 s (inset Figure 4), which was also accompanied by a slight decrease of signal for Pb^{2+} and an increase in the standard deviation for both metals.

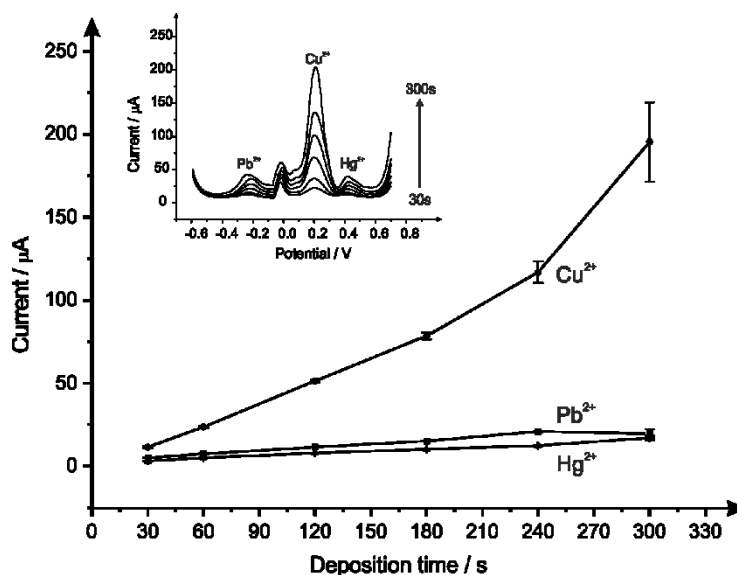


Figure 4. Influence of deposition time on SWASV response to Pb^{2+} , Cu^{2+} and Hg^{2+} in $0.1 \text{ mol L}^{-1} \text{ HCl}$ at a concentration of $50 \mu\text{g L}^{-1}$ of each metal. Inset: Stripping voltammograms obtained for each deposition time assayed between 30 s and 300 s. Pb^{2+} , Cu^{2+} and Hg^{2+} peak potentials corresponded to -0.2 V , $+0.4 \text{ V}$ and $+0.2 \text{ V}$, respectively. SWASV conditions: $+0.7 \text{ V}$ for 15 s conditioning step; 60 s deposition time; 40 mV amplitude; 6 mV step potential; 20 Hz frequency; 10 s equilibration time; 600 rpm stirring speed. Analysis were performed in triplicate ($n = 3$).

We observed that the continuous application of long deposition times under hydrodynamic accumulation on the same SPE in acidic medium (e.g. performing a full calibration analysis on a single sensor) led to a significant loss of sensitivity. In addition, it increased the instability of the signals, due to a noticeable degradation of the gold working electrode and of the silver pseudo-reference electrode. Therefore, considering our focus on real-monitoring application in a high pollution scenario (the Amazon river), the choice of a lower deposition time

was the best compromise for a greater lifetime of the sensor, although the sensitivity was sacrificed. Larger deposition times are instead recommended for applications where maximum sensitivity is required (less polluted conditions), which would justify single uses of the SPE sensor. On these premises, for further analyses, it was preferred to select 60 s as deposition time, although this choice was not associated to the best sensitivity.

During the lab-based experiments, a constant stirring speed of 600 rpm was applied for the conditioning and stripping analysis. To consider conditions that could be more easily transferred into the field, however, the experiments were also performed in quiescent solutions for comparison. Under non-hydrodynamic conditions, similar voltammetric signals were obtained for Pb^{2+} , Cu^{2+} and Hg^{2+} by applying the optimised deposition potential of -0.6 V for 300 s (data not shown). Note that, in absence of stirring, the application of long deposition times does not have any negative effect on the electrodes' surfaces.

3.2. Influence of the electrolyte in the SWASV determination and calibration data

While the pH is a typical parameter that needs to be optimised for the effective detection of heavy metals on gold electrodes, in this work, the working pH was determined by the optimal HCl concentration that would allow the simultaneous detection of Hg^{2+} , Pb^{2+} and Cu^{2+} with clear and distinct peaks. Typically, Hg^{2+} requires hydrochloric acid in solution to promote the accumulation of Hg^{2+} onto the electrode surface [24, 27]. Nonetheless, the effect of hydrochloric acid in solution on the simultaneous determination of Hg^{2+} together with other heavy metals, has not been reported yet. As such, the influence of the electrolyte composition, and in particular of HCl concentrations, on the effectiveness of the simultaneous detection of Cu^{2+} , Pb^{2+} and Hg^{2+} by SPEs was carefully investigated.

Figure 5 shows the results obtained, in terms of Cu^{2+} , Pb^{2+} and Hg^{2+} simultaneous detection, under four HCl concentrations (0.001, 0.01, 0.1 and 1 mol L⁻¹). Regarding the current

values, it was observed that 0.001 mol L⁻¹ was the best performing concentration of HCl for Pb²⁺ detection, while 1 mol L⁻¹ returned the poorest signal. Moreover, Pb²⁺ response did not change much at other HCl concentrations. A good signal for Cu²⁺ detection was observed for all concentrations of HCl, with the highest current intensity obtained in 0.001 mol L⁻¹ HCl, followed by 1 mol L⁻¹. Generally, at high concentrations of HCl, the standard deviations of the responses increased, probably because of a degradation of the SPE surface after the measurements, which was also visually observed. The overall analytical performance in 0.1 mol L⁻¹ resulted in more balanced peak intensities, which can be favourable for further applications, and more stable signals, as reflected by the lower standard deviations of the measurements obtained for all the analytes.

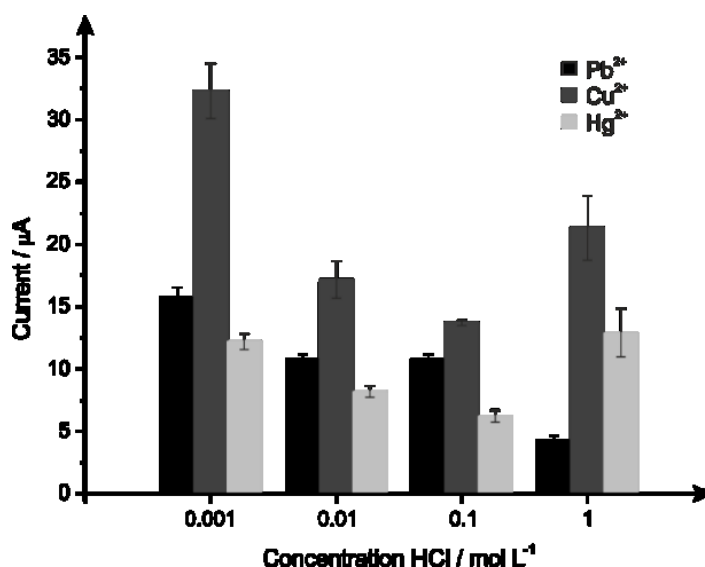


Figure 5. Influence of the electrolyte (i.e. HCl concentration) on the current intensity of stripping voltammetric peaks of 50 μg L⁻¹ of Pb²⁺, Cu²⁺ and Hg²⁺. SWASV conditions: +0.7 V for 15 s conditioning step; -0.6 V deposition potential; 60 s deposition time; 40 mV amplitude; 6 mV step potential; 20 Hz frequency; 10 s equilibration time; 600 rpm stirring speed. Analysis were performed in triplicate (n = 3).

To decide between low (0.001 mol L^{-1}) or mild (0.1 mol L^{-1}) HCl concentration, calibration curves were performed for both electrolyte concentrations. The results obtained are shown in **Figure 5**. It is interesting to note that for each metal, higher sensitivities, defined as current change per unit change of analyte concentration, were obtained in 0.001 mol L^{-1} HCl compared to 0.1 mol L^{-1} HCl, as shown from the slopes of the calibration curves. Nevertheless, a concentration of 0.1 mol L^{-1} HCl led to much wider dynamic linear ranges: $5 - 300 \mu\text{g L}^{-1}$ (**Figure 6A**). On the other hand, in 0.001 mol L^{-1} HCl a significant reduction in the dynamic range was observed for Pb^{2+} and Cu^{2+} , with a linear performance only up to 80 and $120 \mu\text{g L}^{-1}$, respectively (**Figure 6B**). Moreover, greater values of correlation coefficients (R^2) were obtained in 0.1 mol L^{-1} HCl, which allow smaller uncertainties in the predictions of the concentrations of metals in the analysis of unknown samples. In view of these results, an electrolyte concentration of 0.1 mol L^{-1} HCl was selected for further measurements.

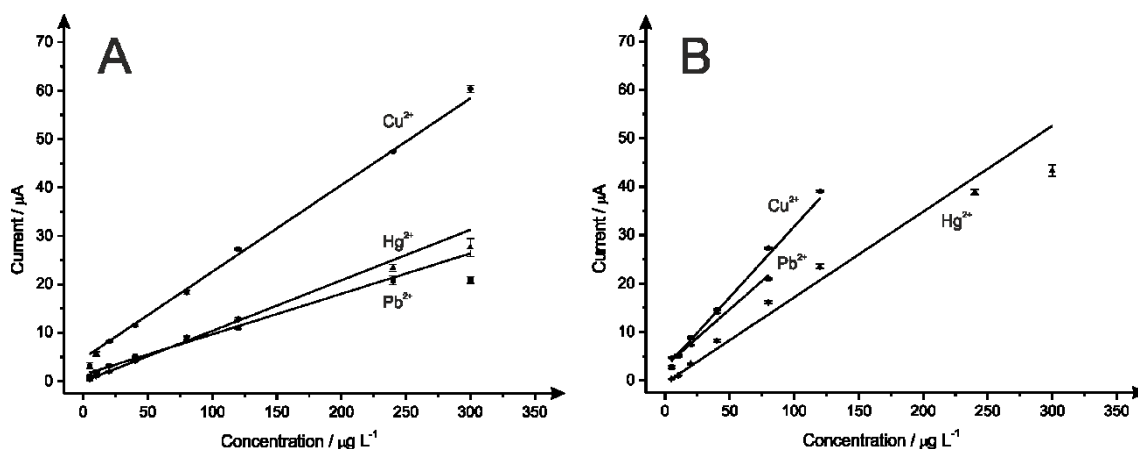


Figure 6. Calibration curves for increasing concentrations of Pb^{2+} , Cu^{2+} and Hg^{2+} ($5-300 \mu\text{g L}^{-1}$) in 0.1 mol L^{-1} HCl (A) and 0.001 mol L^{-1} HCl (B) applying the optimised SWASV method. Analysis were performed in triplicate ($n = 3$). Regression equations at 0.1 mol L^{-1} HCl (A): $y = 0.0685x + 3.4672$, $R^2 = 0.9705$ (Pb^{2+}); $y = 0.193x + 4.3607$, $R^2 = 0.9973$ (Cu^{2+}); $y = 0.0943x + 0.7497$, $R^2 = 0.9919$ (Hg^{2+}). Regression equations at 0.001 mol L^{-1} HCl (B): $y = 0.2377x + 2.9527$, $R^2 = 0.9678$ (Pb^{2+}); $y = 0.3075x + 2.2677$, $R^2 = 0.9978$ (Cu^{2+}); $y = 0.167x + 0.8004$, $R^2 = 0.9835$ (Hg^{2+})

Finally, the reproducibility in the simultaneous determination of the three metals was evaluated. With this purpose, repetitive measurements were performed with a single SPE towards low ($10 \mu\text{g L}^{-1}$) and high concentrations ($60 \mu\text{g L}^{-1}$) of metals in 0.1 mol L^{-1} HCl. As shown in **Figure 7**, a set of 32 consecutive measurements led to good values of the relative standard deviation (RSD) for the three metals (Table 2). Nevertheless, higher RSD values were observed for Hg^{2+} at low concentration (32.6 %). This result might be due to the large differences in current intensities showed by Cu^{2+} at the same concentration. Overall, the results obtained demonstrated great robustness of the developed sensor.

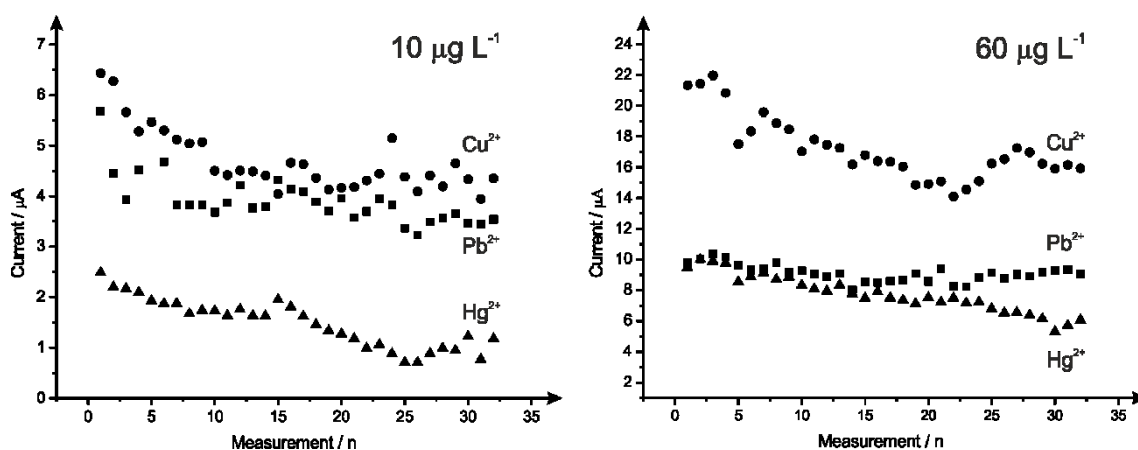


Figure 7. Reproducibility of SWASV determination of low and high concentrations of Pb^{2+} , Cu^{2+} and Hg^{2+} in 0.1 mol L^{-1} on Au SPEs

Table 2 summarises the analytical characteristics of the developed methodology. Very good LODs were achieved with the proposed methodology, even though only a deposition time of 60 s was applied. These values are below the limits established by the Environmental Protection Agency (EPA) in ground water and drinking water [29], which correspond to 0.015, 1.3 and 0.002 mg L^{-1} for Pb^{2+} , Cu^{2+} and Hg^{2+} , respectively. Also, these concentrations meet the requirements established in the EU drinking water Directive [30], which states that 0.010, 2.0 and 0.001 mg L^{-1} for Pb^{2+} , Cu^{2+} and Hg^{2+} , respectively, are safe for human consumption. As such,

the effectiveness of detection of these heavy metals within the levels of concern was demonstrated.

Table 2. Analytical results for the determination of 50 $\mu\text{g L}^{-1}$ Pb^{2+} , Cu^{2+} and Hg^{2+} in 0.1 mol L^{-1} HCl using Au SPEs by applying the optimised SWASV method. Eight replicates of the blank were used for the calculation of LOD and LOQ.

Analytical parameters (n=8)	Metal		
	Pb^{2+}	Cu^{2+}	Hg^{2+}
Slope ($\mu\text{A}/(\mu\text{g L}^{-1})$)	0.0685	0.193	0.0943
R^2	0.9705	0.9973	0.9919
LOD ($\mu\text{g L}^{-1}$)	2.2	1.5	1.3
LOQ ($\mu\text{g L}^{-1}$)	7.3	5.1	4.3
Dynamic Linear Range ($\mu\text{g L}^{-1}$)	5 - 300		
RSD (%) 10 $\mu\text{g L}^{-1}$	13.7	13.1	32.6
RSD (%) 60 $\mu\text{g L}^{-1}$	6.1	11.9	15.8

Additionally, Table 3 compares the analytical performance of the proposed methodology with other gold-based electrodes reported in the literature for the detection of the same heavy metals in water samples. Although a direct comparison is difficult considering the different matrix analysed in each study, our study demonstrates a wide detection range and good low limits of detection.

Table 3. Detection of Pb²⁺, Cu²⁺, and Hg²⁺ in water samples with gold-based electrodes: comparison of performance

Gold-based electrodes	Analytes	Matrix	LOD (µg L ⁻¹)	Linear range (µg L ⁻¹)	Reference
AuND@GPL ^a	Pb ²⁺ , Cu ²⁺ , Hg ²⁺	Lake water	Pb ²⁺ : 0.12 Cu ²⁺ : 0.19 Hg ²⁺ : 0.18	0 - 50	[31]
AuNS-modified CPSPE ^b	As ³⁺ , Hg ²⁺ , Pb ²⁺	Ground water	As ³⁺ : 3.57 Hg ²⁺ : 11.08 Pb ²⁺ : 20.55	As ³⁺ : 10.8 – 419.4 Hg ²⁺ : 33.6 – 361.5 Pb ²⁺ : 62.3 – 215.6	[32]
Au SPGE-HT ^c	Hg ²⁺	Waste water and rain water	Hg ²⁺ : 1.1	0 - 30	[24]
AuNPs/S-C ^d	Cu ²⁺ , Hg ²⁺	Lake water	Cu ²⁺ : 0.19 Hg ²⁺ : 1.4	Cu ²⁺ : 0.64 – 63.55 Hg ²⁺ : 4.01 – 300.89	[33]
Bi/AuNPs film SPCE ^e	Zn ²⁺ , Pb ²⁺ , Cu ²⁺	Deionised water	Zn ²⁺ : 0.06 Pb ²⁺ : 0.03 Cu ²⁺ : 0.03	1 - 150	[34]
CNF/AuNPs SPCE ^f	Hg ²⁺	River water	Hg ²⁺ : 6.0	20 - 240	[35]
AuNPs SPGE ^g	Pb ²⁺ , Cu ²⁺	Deionised water	Pb ²⁺ : 2.2 Cu ²⁺ : 1.6	Pb ²⁺ : 20 - 200 Cu ²⁺ : 20 – 300	[36]
AuNPs SPCE arrays ^h	Pb ²⁺ , Cu ²⁺	Deionised water	Pb ²⁺ : 2.1 Cu ²⁺ : 1.4	Pb ²⁺ : 10 - 100 Cu ²⁺ : 10 - 150	[37]
AuNPs SPCE ⁱ	Hg ²⁺	Ground water	Hg ²⁺ : 1.02	1 - 100	[38]
Au SPGE-LT ^j	Pb ²⁺ , Cu ²⁺ , Hg ²⁺	<i>In situ</i> River water	Pb ²⁺ : 2.2 Cu ²⁺ : 1.5 Hg ²⁺ : 1.3	5 - 300	This work

^aGold nanodendrite - graphite pencil lead electrode; ^bGold nanostar screen-printed carbon electrode; ^cHigh temperature gold-cured screen-printed electrode; ^dGold nanoparticles dotted S-doped carbon nanoflakes electrode; ^eIn-situ bismuth – gold nanoparticles film screen-printed carbon electrode; ^fCarbon nanofibres-gold nanoparticles screen-printed carbon electrode; ^gGold nanoparticles screen-printed gold electrodes; ^hGold nanoparticles screen-printed carbon electrode arrays; ⁱGold nanoparticles screen-printed carbon electrodes; ^jLow temperature gold-cured screen-printed electrode

3.3. Interferences study and field tests in the Amazon river

Once the detection methodology was developed and optimised in the lab, the potential interference of other metals that can be found in real water samples on the SPEs was tested. As shown in **Figure S3**, the quantification of 20 µg L⁻¹ of Pb²⁺, Cu²⁺ and Hg²⁺ in 0.1 mol L⁻¹ HCl is

performed in the presence of $20\ \mu\text{g L}^{-1}$ of Cd^{2+} , Zn^{2+} , Se^{4+} , Mo^{3+} and Bi^{3+} . It is interesting to note that the presence of Cd^{2+} causes an additive effect in the Pb^{2+} peak. This outcome can be the result of similarities in the potential peak of both heavy metals in gold-based electrodes. Probably for the same reason, the presence of Se^{4+} leads to a significant reduction of the Hg^{2+} peak. Moreover, the presence of Zn^{2+} in solution has a noticeable influence in their voltammetric response of Pb^{2+} , Cu^{2+} and Hg^{2+} , with a decrease in the relative peak currents of approximately 30%. Finally, the peak potential corresponding to Bi^{3+} , which appears around 0.2 V, interferes with the voltammetric peaks corresponding to Cu^{2+} and Hg^{2+} , thus causing a slight reduction in their current peak intensities. Nonetheless, these results demonstrate that the presence of these interference do not compromise the selectivity of our developed methodology towards the three target heavy metals.

Then, SPEs were applied in real environmental monitoring of water in two different points along the Amazon river (Aguila and Santa Sofia), Colombian side, to demonstrate their applicability under extreme conditions of temperature and humidity. No pre-treatment of the samples was carried out apart from the addition of HCl up to the concentration of $0.1\ \text{mol L}^{-1}$, as previously optimised.

Figures 8A and 8C shows the voltammograms obtained for the analysis in field of Pb^{2+} , Cu^{2+} and Hg^{2+} in the two sampling points of the Amazon river and the subsequent calibration curves for the standard addition method to obtain quantitative measurements (Figures 8B and 8D). As shown in Figure 8, voltammetric peaks of metals were clearly identified in water samples and current intensities increased with the standard addition method. The successful quantification of the three metals investigated could be achieved in both samples. In the sample from Aguila (Figure 8A), a shift in the potential of the stripping peaks of Pb^{2+} and Cu^{2+} between the real water sample and additions was observed, which was also noticeable in the voltammetric peak of Pb^{2+} in the water from Santa Sofia (Figure 8C). This behaviour has been reported before in the analysis of spiked fuel bioethanol (hydroethanolic solutions), but no

explanation was found [25]. In agreement with the same report [25], a constant peak appears also in the voltammograms at potential around 0.0 V, which is visible in the blank and does not increase with the additions. This peak could be related to a contamination presents in the electrolyte solution derived from the degradation of the silver pseudo-reference electrode printed on the electrochemical platform.

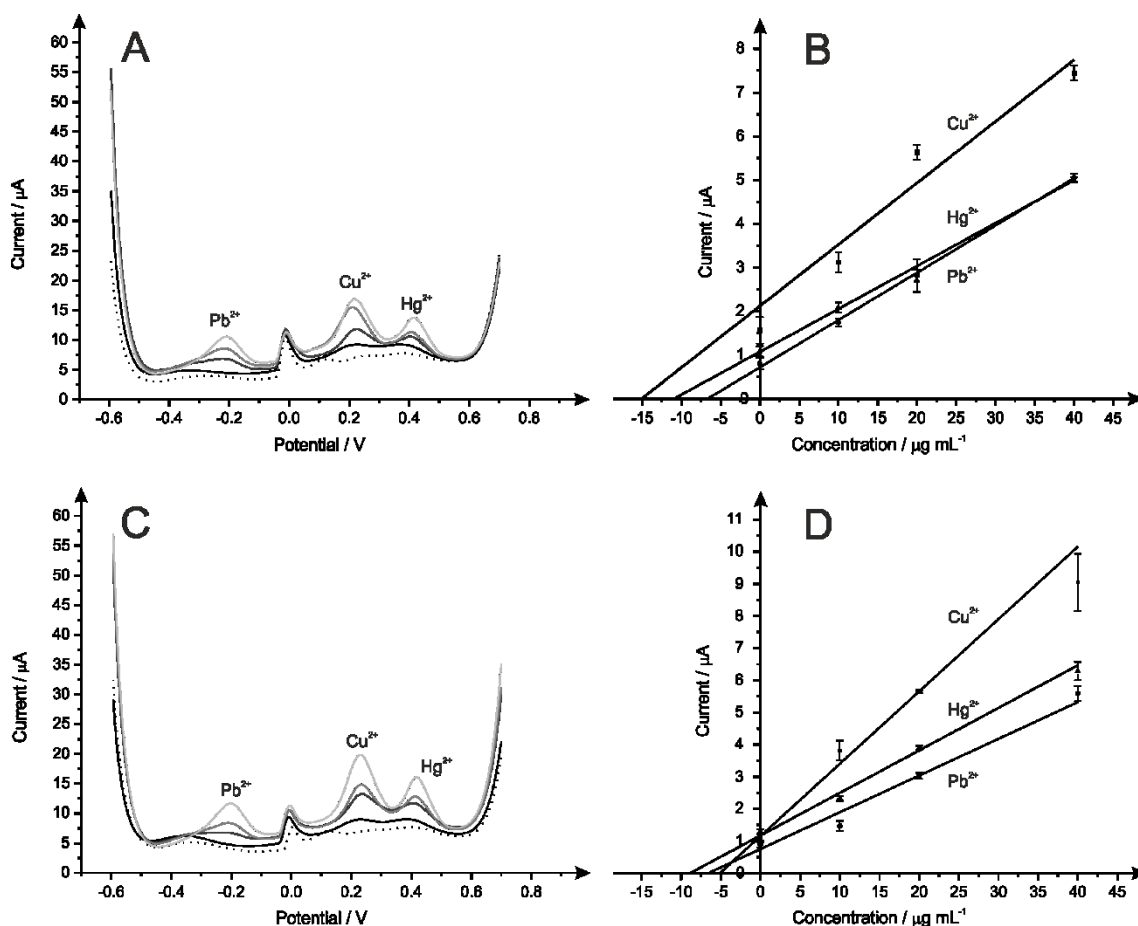


Figure 8. SWASV recordings for the on-site multi-detection of Pb^{2+} , Cu^{2+} and Hg^{2+} in water samples from the Amazon river collected in the indigenous communities of Aguila (A) and Santa Sofia (C). Voltammetric curves are displayed in this order: blank (dot line), real water sample (black line), first, second and third additions (grey lines). Calibration curves obtained with the additions of standard solution of the three metals at 10, 20 and 40 $\mu g L^{-1}$ in real water samples from Aguila (B) and Santa Sofia (D).

Table 4 summarises the results obtained for the on-site analysis of the target heavy metals in water samples by the proposed SWASV method, along with their validation with different analytical techniques. The results are expressed as the mean of three replicates with their deviations associated to the quantification with standard addition method at 95% confidence level. Concentrations of Pb^{2+} , Cu^{2+} and Hg^{2+} were higher in the Aguila community, probably due to its closest location to the city of Leticia and the consequent influence of port activities in the water pollution. Also, higher values of standard additions of SWASV measurements were observed in this location, which could be related to the high level of turbidity of the samples that might interfere in the accuracy of the measurement. Concerning the results obtained for Hg^{2+} , high concentrations of this metal were detected in both locations, which exceeded the maximum limit of $2 \mu\text{g L}^{-1}$ established by EPA for drinking water.

Table 4. Heavy metals detection in field by the proposed SWASV method and validation by ICP-OES and CVAAS

Aguila			
Concentration of metals (n=3) ($\mu\text{g L}^{-1}$)			
	SWASV	ICP-OES	CV-AAS*
Pb^{2+}	6.87 ± 2.27	8	-
Cu^{2+}	12.2 ± 5.38	< 8	-
Hg^{2+}	10.6 ± 3.00	< 20	-
Santa Sofia			
Concentration of metals (n=3) ($\mu\text{g L}^{-1}$)			
	SWASV	ICP-OES	CV-AAS
Pb^{2+}	5.00 ± 2.84	4	-
Cu^{2+}	7.72 ± 3.66	< 8	-

Hg²⁺	9.63 ± 1.96	< 20	6.7 ± 0.8
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* Note that the analysis of Hg²⁺ could not be performed in the sample from Aguila because the amount of sample left was not enough to assure the correct analysis.

To ensure reliability in the measurements and prevent any false positives/negatives caused by contamination, the electrodes were used for single measurements. Future work should, however, focus on the development of biodegradable electrodes that would limit any damage to the environment caused by single use, as well as on effective strategies, compatible with field applications, to clean the electrodes for their re-utilisation.

To validate the proposed SWASV methodology, water samples from the two locations tested were analysed in a centralised laboratory for comparative purposes. As reported in Table 3, a good agreement was found for all metals between ICP-OES and SWASV, even though the concentration of Cu²⁺ and Hg²⁺ in water were found around the LOD of the technique. Moreover, the concentration of Hg²⁺ in the water sample collected in Santa Sofia was confirmed in the laboratory by CVAAS, which presents better LOD for Hg²⁺ quantification, and a very good agreement with the value determined by SWASV was observed.

4. Conclusions

Effective monitoring of water quality in remote areas, such as the Amazon, is hampered by the lack of affordable and robust sensing tools. In this context, this work presents the development and application of an effective electrochemical methodology for the direct and simultaneous determination of Pb²⁺, Cu²⁺ and Hg²⁺ in environmental waters. Both the deposition potential and time in the voltammetric method implemented were optimised for the simultaneous detection of the target metals, and the influence of the HCl concentration in the electrolyte was also investigated. Our methodology showed a very good analytical performance in the optimised conditions, in terms of wide linear range, LOD below EPA guidelines and good

reproducibility and stability, which clearly demonstrated its suitability for further environmental applications. Finally, the developed methodology was successfully implemented in the field to monitor, for the first time, the selected heavy metals in the Amazon river. Water samples were freshly collected and analysed on-site without any pre-treatment. The measurements were validated in a centralised analytical laboratory, thus confirming the effective quantifications of the three toxic heavy metals in water with the method developed and its great potential for real environmental monitoring applications.

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